

The University of Chicago

REACTIONS OF FREE RADICALS IN SOLUTION

A DISSERTATION SUBMITTED TO THE FACULTY OF
THE DIVISION OF THE PHYSICAL SCIENCES IN
CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY
DECEMBER, 1946

By
HAROLD NATHANIEL GRAHAM

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ACKNOWLEDGMENT

The author wishes to acknowledge with gratitude the inspiration and guidance given by Professor M. S. Kharasch during the course of this investigation. He is also indebted to Professor F. H. Westheimer and Dr. W. H. Urry.

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PART I

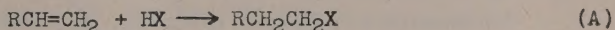
ADDITIONS OF MERCAPTANS TO OLEFINS

INTRODUCTION

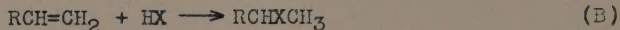
The work described in this paper was undertaken in connection with a government project, the object of which was the investigation of the mechanism of the polymerizations and copolymerizations used in the preparation of synthetic rubber. Since a number of workers were employed on this project, it has proven necessary, in order to give a clear account of the results obtained, to include both in the theoretical and experimental parts, certain results for which the author is only partially responsible.¹

It was believed that the mercaptans used to promote the polymerization of the hydrocarbons (butadiene and styrene) in the production of GR-S, function as chain transfer agents. That is to say, they add to the unsaturated hydrocarbons as free radicals, thereby producing new radicals which continue this process and thus form the characteristic product of high molecular weight. Hence, it became of interest to study the additions of various mercaptans to the olefins in question.

The directed addition of reagents of the type HX to unsymmetrical olefin derivatives has been the subject of many investigations. Two reactions are theoretically possible:

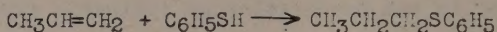


¹Acknowledgment is here made to Messrs. R. M. Adams, T. H. Meltzer, and Everett Rauh, as well as to Dr. Walter Nudenberg for some of the material used in the preparation of this thesis.



Markownikoff, who investigated many such reactions, developed the rule that the negative radical X always adds to the carbon atom carrying the smaller number of hydrogen atoms (Reaction B).¹ Exceptions to this rule were later found, and it has become customary to call additions which proceed as indicated by Markownikoff's rule "normal" whereas those which give the other product are called "abnormal."

In 1905 Posner added mercaptans (RSH) to unsymmetrical olefins and obtained abnormal products,² for example:



This abnormal behavior of mercaptans was later explained by Kharasch who assumed that the addition reactions in question proceeded by a chain mechanism involving free radicals.³ Further evidence to support this theory has been obtained in the course of the work hereafter described. First, however, there is presented a review of the subject of chain reactions and their occurrence during the addition of certain reagents to olefinic derivatives.

¹Markownikoff, Compt. rend. 81, 670 (1875).

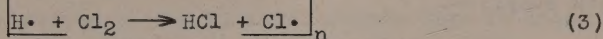
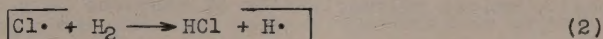
²Posner, Ber. 38, 646 (1905).

³Kharasch, Read, and Mayo, Chem. and Ind. 57, 752 (1938).

HISTORICAL REVIEW

Chain Reactions in the Gaseous Phase

Chain reactions involving atoms or free radicals were first postulated to explain the apparent failure of Einstein's Law of Photochemical Equivalence.¹ For example, in the photo-combination of hydrogen and chlorine,² the number of molecules of hydrogen chloride formed per quantum of light energy absorbed is large--that is to say, the quantum yield is far greater than unity. Further work showed that Einstein's quantum relation can be properly applied only to the first stage of the reaction in question (Equation (1)).



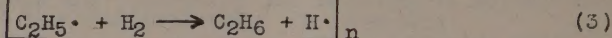
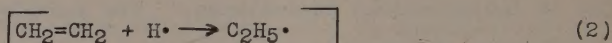
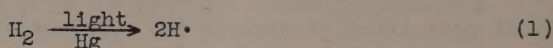
Equations (2) and (3) constitute one cycle of a chain reaction. Since this cycle may be repeated many times before the chain is finally broken, the high quantum yield is readily explained. Similar effects in many other vapor phase reactions³ (for example, the decomposition of hydrogen chloride or hydrogen bromide and the chlorination of carbon monoxide or sulfur dioxide) have also been accounted for by chain mechanisms.

¹Einstein, Ann. Physik. 37, 832 (1912).

²Allmand, Trans. Far. Soc. 21, 444 (1925).

³Rice and Rice, The Aliphatic Free Radicals, The Johns Hopkins Press, Baltimore, Md. (1935).

The first organic reaction to be explained by a chain mechanism was the photo-chemical hydrogenation of ethylene in the presence of mercury vapor.¹ Here the number of molecules of ethane formed is far in excess of the number of light energy quanta absorbed. For this reaction, Taylor in 1925 postulated the following mechanism:



Here again reactions (2) and (3) constitute one cycle of a chain reaction, and Einstein's law applies only to equation (1). Since the two latter reactions are both exothermic, the proposed mechanism is thermodynamically possible. Taylor also proposed a chain mechanism² to explain the high quantum yields observed for the photochemical polymerization of ethylene in a mixture of hydrogen and ethylene.

Since Taylor's work, the thermal and photochemical decompositions of many hydrocarbons, aldehydes, ketones, ethers, and azo-compounds have been shown³ to proceed by chain mechanisms. The decomposition of butane at 525° is a reaction of this type.⁴ At that temperature pure butane decomposes very slowly. But if a small quantity of mercury dimethyl is introduced, 20 molecules of butane are decomposed for each molecule of mercury dimethyl decomposed.

¹Taylor, Trans. Far. Soc. 21, 560 (1925).

²Taylor and Jones, J. A. C. S. 52, 1111 (1930).

³Rice and Rice, op. cit.

⁴Frey, Ind. Eng. Chem. 26, 200 (1934).



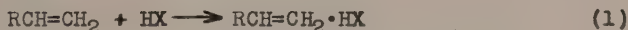
The free methyl radicals which are formed then attack the butane. Similarly, acetaldehyde, in the presence of a trace of azomethane, decomposes at a temperature at which the pure substance is stable.¹ The chain length is about 30--that is, about 30 molecules of aldehyde disappear per molecule of azomethane decomposed.

Chain Reactions in Solution

A. Addition of HCl and HI to Olefins

When hydrogen chloride and hydrogen iodide are added to unsymmetrical olefins, the addition product obtained is, in almost every instance, the normal one--that is, the one predicted by Markownikoff's rule. Anhydrous ferric and aluminum chlorides are excellent catalysts for such normal additions.² The addition of hydrogen iodide is also catalyzed by iodine.

A possible mechanism for these normal additions is given below. It has been shown that the rate of the reaction depends more on the concentration of the hydrogen halide than it does on the concentration of the olefin.³ Hence, the first step postulated is the formation of a molecular complex between these two components.



This complex adds a negative halide ion formed by the partial dissociation of the hydrogen halide in the polar solvent. The

¹Sickman and Allen, J. A. C. S. 56, 125 (1934).

²Marasch, Kleiger, and Mayo, J. Org. Chem. 4, 428 (1939).

³Coffin and Maas, Can. J. Research 3, 526 (1930), Halder and Maas, ibid., 16B, 453 (1938), Maas and Sivertz, J. A. C. S. 47, 2883 (1925).

addition takes place at the more positive of the two carbon atoms joined by the double bond--that is, the one carrying the smallest number of hydrogen atoms.

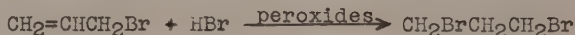


Finally the negative carbanion adds a proton.



B. Addition of HBr to Olefins

When hydrogen bromide is added to allyl bromide ($CH_2=CHCH_2Br$), various products ranging from almost pure 1,2-dibromopropane to almost pure 1,3-dibromopropane are obtained. The reaction in question was intensively studied by Kharasch and Mayo,¹ who in 1931 discovered that oxygen and peroxides direct the addition contrary to Markownikoff's rule. This influence is known as the "peroxide effect."



Kharasch and Mayo found that the normal addition product is formed exclusively when the reaction is carried out in vacuo in the dark and with freshly prepared reagents. A trace of oxygen in the system, or of peroxides in the allyl bromide, is sufficient to cause the formation of some abnormal adduct. Later it was shown that most ethylenic and acetelenic compounds show the peroxide effect when treated with hydrogen bromide. Derivatives of crotonic and acrylic acids are exceptions.²

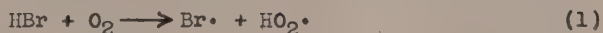
¹Kharasch and Mayo, J. A. C. S. 55, 2468 (1933), 60, 3097 (1938).

²Kharasch and McNab, Unpublished work; Walling, Kharasch, and Mayo, J. A. C. S. 61, 2693 (1939).

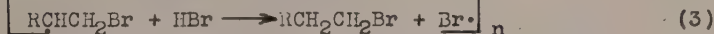
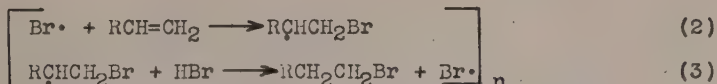
About one mol per cent of benzoyl peroxide or of ascaridol is often used to bring about abnormal additions. Oxygen and peroxides (which form in olefins when these substances are exposed to air) are also effective. Antioxidants such as hydroquinone, catechol, thiophenol, diphenylamine, and nitric oxide effectively inhibit many peroxide-catalyzed additions.

Since traces of peroxides are sufficient to produce abnormal additions,¹ and since small quantities of antioxidants inhibit them, Kharasch and his co-workers chose to explain these additions by chain mechanisms. It was necessary to account first for the fact that, among the halogen acids, only hydrogen bromide gives the abnormal additional products, and then to explain how the chains are started, and why a chain mechanism leads to an abnormal adduct.

Since only one halogen acid shows the peroxide effect, the oxidant must act on that substance (hydrogen bromide) rather than on the olefin. Undissociated bromine molecules (reaction in the dark) do not catalyze abnormal addition, so it was assumed that the first step in the abnormal reaction is the oxidation of hydrogen bromide to bromine atoms (Equation (1)).



It has been shown that the oxidation of hydrogen bromide by oxygen, although ordinarily slow, is greatly accelerated by olefinic compounds.²



¹Mayo and Walling, Chem. Reviews, 27, 370 (1940).

²Urishibara and Simamura, Bull. Chem. Soc. Japan, 14, 323 (1934).

Equations (2) and (3) represent one cycle in a typical chain reaction.

It remains to explain why the bromine atom adds contrary to Markownikoff's rule. Undoubtedly, of the two free radicals which might be formed, the one actually produced is the more stable--that is, the one with the lowest energy content. And almost all that is known about such free radicals indicates that their stabilities fall in the following order:

tertiary > secondary > primary

The exceptional behavior of acrylic acid and acrylic esters indicate that the free radical $\cdot\text{CH}_2\text{CHBrCOOH}$ is more stable than the free radical $\text{BrCH}_2\dot{\text{C}}\text{HCOOH}$ --probably because the first is more easily stabilized by the formation of resonance hybrids. If this assumption is correct, the peroxide catalyzed addition of hydrogen bromide to acrylic acid should proceed by a mechanism different from that of the normal addition even though the two reactions yield the same product.

A chain reaction can include no step which is highly endothermic. The oxidation of hydrogen bromide (Equation (1)) meets this condition, whereas the similar oxidations of hydrogen chloride and hydrogen fluoride probably do not. The addition of a free halogen atom (Equation (2)) is exothermic (and hence perfectly feasible) for fluorine, chlorine, and bromine. But the rupture of the hydrogen halide bond (Equation (3)) is endothermic for fluorine and chlorine, whereas, for bromine, the energy involved is practically zero. Hence, of the three reactions postulated, (1) and (3) could not occur if the halogen were either chlorine or fluorine. Hydrogen iodide is very easily oxidized to iodine which is a specific catalyst for the normal addition reaction.

Moreover, with hydrogen iodide, the reaction corresponding to Equation (2) is slightly endothermic. For both of these reasons, abnormal additions of hydrogen iodide are not to be expected.

Rate studies have shown that, for the addition of hydrogen bromide, the normal and abnormal reactions are independent and competing. The peroxide effect is most noticeable when the normal addition is slow; here the abnormal addition can predominate even in the presence of an antioxidant. Addition to 1-bromopropene¹ is an example of this type of reaction. Where the normal addition is rapid, an antioxidant is sufficient to retard the abnormal reaction. The additions of vinyl chloride and bromide are of this type.² Where the normal addition is extremely rapid, oxygen alone is insufficient to cause the peroxide effect, and considerable quantities of peroxide must be added. The additions to propylene and isobutylene fall in this category.³ With 2-bromo-2-butene the normal addition is extremely rapid,⁴ and since it is of higher order than the abnormal addition, it is more retarded by dilution of the reaction mixture with an inert solvent. Hence in this instance it is necessary to add such a diluent and to use an oxidant (air) in order to obtain a good yield of abnormal product. Even under these conditions 20 per cent of the normal product is obtained.

C. Abnormal Addition of Bisulfites

Kharasch and his co-workers added bisulfites to ethylene,

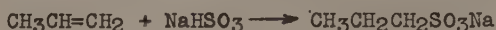
¹Kharasch, Engelmann, and Mayo, J. Org. Chem. 2, 288, 400, 577 (1937).

²Kharasch, McNab, and Mayo, J. A. C. S. 55, 2521 (1933); Kharasch and Hannum, ibid. 56, 712 (1934).

³Kharasch and Hinckley, J. A. C. S. 56, 1243 (1934); Kharasch, McNab, and Mayo, op. cit.

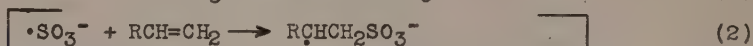
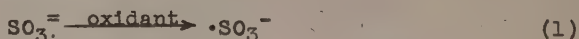
⁴Walling, Kharasch, and Mayo, op. cit.

propylene and isobutylene.¹ Reaction occurs only in the presence of oxygen, and the abnormal product is the only substance formed.

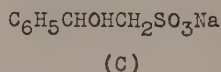
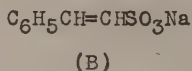
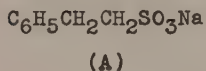


Schenck found that, in many instances, an increase of the oxygen pressure above 30 mm. decreases the yield of addition product.² Antioxidants prevent addition,¹ and agents such as sodium or ammonium nitrites which oxidize bisulfites resemble oxygen in promoting the reaction. Bäckström showed that the oxidation of the bisulfite ion is a chain reaction involving the free $\text{HSO}_3\cdot$ radical.³

Kharasch, May, and Mayo were led by the evidence first cited to suggest the following chain mechanism for the addition of bisulfites to olefins.⁴



In the presence of oxygen, bisulfites add to styrene to give three products:⁵



All of these substances can be formed from the free radical

¹Kharasch, May, and Mayo, J. Org. Chem. 3, 175 (1938), Grigorjeff, Doctor's Dissertation, University of Chicago, 1939.

²Schenck, Doctor's Dissertation, University of Chicago (1940).

³Bäckström, Z. physiks. Chem. B25, 122 (1934).

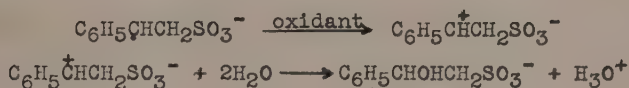
⁴Kharasch, May, and Mayo, op. cit.

⁵Kharasch, Schenck, and Mayo, J. A. C. S. 61, 3092 (1939).

postulated as the product of reaction (2). The abnormal addition product (A) is formed by reaction (3). The unsaturated compound (B) may be formed by reaction of oxygen with the product of reaction (2):



Oxygen is the only oxidizing agent which reacts in this way. The hydroxy compound (C) is formed in the presence of oxygen, nitrites or persulfates and other oxidizing agents. Its formation may be represented by the following reactions:



D. Abnormal Addition of Mercaptans

The early work of Posner¹ on the addition of mercaptans to olefins which showed that the abnormal products are obtained has been corroborated by Ashworth and Burkhardt who added thiophenol to styrene.² Burkhardt observed that the reaction is greatly accelerated by light and thought that the "active agent must have the sulphur in a positive ion or in an oxidizing form;" the oxidizing agent, he suggested, might be a free radical operating through a chain mechanism.³

Mercaptans are similar to hydrogen bromide in that they give both normal and abnormal additional products with olefinic compounds. Hydrogen sulfide at temperatures below 200° gives only the normal products.⁴ Sulfur is a catalyst for this addition.

¹Posner, *Per.* 38, 646 (1905).

²Ashworth and Burkhardt, *J. Chem. Soc.* 1928, 1791.

³Burkhardt, *Trans. Far. Soc.* 30, 18 (1934).

⁴Ipatieff and Friedman, *J. A. C. S.* 61, 71 (1939), Jones and Ried, *J. A. C. S.* 60, 2452 (1938), Jones, Doctor's Dissertation, Johns Hopkins University (1936).

Mercaptans usually give the abnormal product when no catalysts (such as sulfuric acid or sulfur) are present. Mayo and Walling regard the acid-catalyzed reaction as analogous to the reaction of hydrogen halide with the halogen acid complex of the olefin (cf. Equation (1), page 4). The sulfur catalysis they regard as analogous to the iodine catalysis in the normal addition of hydrogen iodide to olefins.

Table 1 summarizes a number of normal addition of mercaptans to unsaturated hydrocarbons. Some of the sulfides listed as products were prepared by Reid and Jones who treated olefins with hydrogen sulfide. This compound adds normally to the olefin in the presence of sulfur, and the mercaptan formed then adds normally to another molecule of the olefin to give the indicated sulfide.

Holmberg reported that thioglycolic acid adds abnormally to styrene.¹ Kharasch found that at 25° in vacuo, in the presence of hydroquinone, no reaction between these compounds occurs within 50 hours.² In the presence of ascaridol, however, thioglycolic acid adds abnormally to styrene within a few minutes. This abnormal reaction has been shown to be catalyzed by oxygen and peroxides, accelerated by light, and inhibited by antioxidants. These similarities to the abnormal addition of hydrogen bromide strongly suggest that the reaction goes by a chain mechanism involving the free mercaptyl radical. The first definite proposal of such a chain mechanism was made by Kharasch, Read, and Mayo:³



¹Holmberg, J. Prak. Chem. 141, 104 (1934).

²Kharasch, Read, and Mayo, op. cit.

³Ibid.

TABLE 1

NORMAL ADDITION OF MERCAPTANS TO OLEFINS

Olefin	Mercaptan	Product	Reference
$\text{CH}_2=\text{CH}_2$	$\text{C}_2\text{H}_5\text{SH}$	$\text{CH}_3\text{CH}_2\text{SC}_2\text{H}_5$	1
$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{C}_2\text{H}_5\text{SH}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{SC}_2\text{H}_5$	1
$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{SC}_6\text{H}_5$	1
$\text{CH}_3\text{CH}=\text{CH}_2$	$(\text{CH}_3)_2\text{CHSH}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{SCH}(\text{CH}_3)_2$	1
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{SC}_6\text{H}_5$	3
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	$(\text{CH}_3)_3\text{CSH}$	$(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{SC}(\text{CH}_3)_3$	2
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$\text{C}_6\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{SC}_6\text{H}_5$	3
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}_2$	$\text{C}_2\text{H}_5\text{SH}$	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CH}_3)\text{SC}_2\text{H}_5$	1
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}_2$	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_5\text{SH}$	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CH}_3)\text{SR}^{(A)}$	1
Cyclohexene	Cyclohexyl-SH	Dicyclohexyl sulfide	1
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}_2$	p-thiocresol	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}(\text{CH}_3)\text{SR}^{(B)}$	1
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}(\text{CH}_3)\text{SC}_6\text{H}_5$	1
$n\text{-C}_4\text{H}_9\text{C}\equiv\text{CH}$	$\text{C}_2\text{H}_5\text{SH}$	$n\text{-C}_4\text{H}_9\text{C}(\text{SC}_2\text{H}_5)=\text{CH}_2$	1

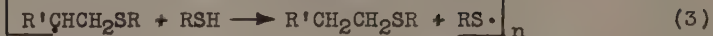
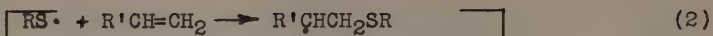
$(A)_R$ = iso-octyl group

$(B)_R$ = p-tolyl group

¹Jones and Reid, op. cit.

²Allen, U. S. Patent, Chem. Abstracts, 30, 6760 (1936).

³Ipatieff, Pines, and Friedman, J. A. C. S. 60, 2731 (1938).



It has been noted by Mayo and Walling that the heats of reaction involved in this mechanism are similar to those involved in the abnormal addition of hydrogen bromide. The easy oxidation of mercaptans to disulfides and the ready dissociation of disulfides to free radicals further supports this mechanism.

Table 2 summarizes many of the reported abnormal additions of mercaptans to unsaturated hydrocarbons.

TABLE 2

ABNORMAL ADDITIONS OF MERCAPTANS TO OLEFINS

Olefin	Mercaptan	Product	Reference
$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$	1
$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{C}_2\text{H}_5\text{SH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SC}_2\text{H}_5$	2
$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{CH}_3\text{C}(=\text{O})\text{SH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SCOCH}_3$	2
$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_5$	3
$\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_5$	3
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	$\text{C}_2\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{SC}_2\text{H}_5$	2
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{SC}_6\text{H}_5$	3
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	$n\text{-C}_4\text{H}_9\text{SH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{SC}_4\text{H}_9$	2
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	$\text{CH}_3\text{C}(=\text{O})\text{SH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{SCOCH}_3$	2
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$\text{C}_2\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{SC}_2\text{H}_5$	2, 1
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$\text{C}_6\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{SC}_6\text{H}_5$	3, 1
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{SCH}_2\text{C}_6\text{H}_5$	1
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	$\text{CH}_3\text{C}(=\text{O})\text{SH}$	$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{SCOCH}_3$	2
$(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$	$\text{C}_2\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{SC}_2\text{H}_5$	2
$(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{SC}_6\text{H}_5$	3
$(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$	$\text{CH}_3\text{C}(=\text{O})\text{SH}$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{SCOCH}_3$	2
$n\text{-C}_3\text{H}_7\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_5\text{SH}$	$n\text{-C}_3\text{H}_7\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_5$	3
$n\text{-C}_9\text{H}_{19}\text{CH}=\text{CH}_2$	(with each of: $\text{C}_6\text{H}_5\text{SH}$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}$ $\alpha\text{-C}_{10}\text{H}_7\text{SH}$ $n\text{-C}_{12}\text{H}_{25}\text{SH}$	$n\text{-C}_n\text{H}_{2n-1}\text{CH}_2\text{CH}_2\text{SR}^{(\text{A})}$	4
$n\text{-C}_{11}\text{H}_{23}\text{CH}=\text{CH}_2$			
$n\text{-C}_{13}\text{H}_{27}\text{CH}=\text{CH}_2$			
$n\text{-C}_{15}\text{H}_{31}\text{CH}=\text{CH}_2$			
$n\text{-C}_{17}\text{H}_{35}\text{CH}=\text{CH}_2$			
$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	$p\text{-C}_6\text{H}_5\text{-}p\text{-C}_6\text{H}_4\text{SH}$	$n\text{-C}_4\text{H}_9\text{CH}_2\text{CH}_2\text{SR}^{(\text{B})}$	5
$n\text{-C}_5\text{H}_{11}\text{CH}=\text{CH}_2$	$p\text{-C}_6\text{H}_5\text{-}p\text{-C}_6\text{H}_4\text{SH}$	$n\text{-C}_5\text{H}_{11}\text{CH}_2\text{CH}_2\text{SR}^{(\text{B})}$	5
$n\text{-C}_{13}\text{H}_{27}\text{CH}=\text{CH}_2$	$p\text{-C}_6\text{H}_5\text{-}p\text{-C}_6\text{H}_4\text{SH}$	$n\text{-C}_{13}\text{H}_{27}\text{CH}_2\text{CH}_2\text{SR}^{(\text{B})}$	5

TABLE 2--Continued

Olefin	Mercaptan	Product	Refer- ence
$C_6H_5CH=CH_2$	C_6H_5SH	$C_6H_5CH_2CH_2SC_6H_5$	1
$C_6H_5CH=CH_2$	CH_3SH	$C_6H_5CH_2CH_2SCH_3$	7
$C_6H_5CH=CH_2$	$SHCH_2COOH$	$C_6H_5CH_2CH_2SCH_2COOH$	6
$C_6H_5CH=CH_2$	$CH_3C(=O)SH$	$C_6H_5CH_2CH_2SCOCH_3$	8

(A)_R = groups which are attached to the sulfur atom in the four mercaptans indicated.

(B)_R = p-diphenyl group.

¹Posner, op. cit.

²Ipatieff and Friedman, op. cit.

³Ipatieff, Pines, and Friedman, op. cit.

⁴Reid and Jones, op. cit.

⁵Lester, Rodgers, and Reid, J. A. C. S. 66, 1674 (1944).

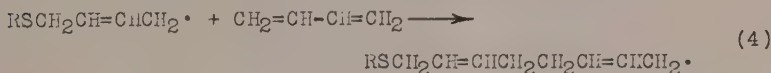
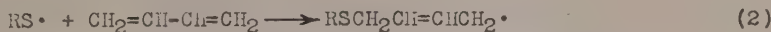
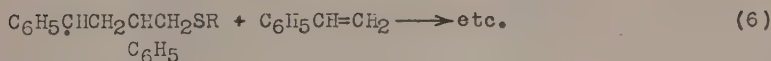
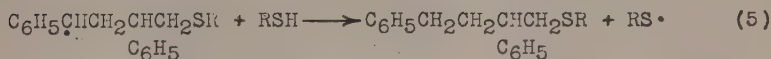
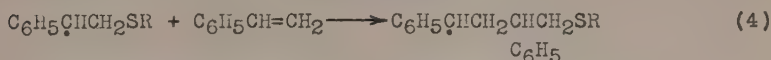
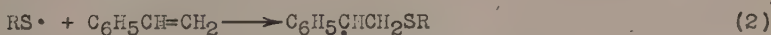
⁶Holmberg, op. cit.

⁷Kaneko and Mii, Chem. Abstracts, 33, 2106 (1939).

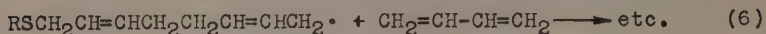
⁸Holmberg, Chem. Abstracts, 32, 4151 (1938).

DISCUSSION OF RESULTS

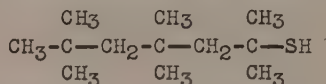
When a mercaptan is added to butadiene or to styrene, a number of addition products are formed. In one of these products the molecular ratio of hydrocarbon to mercaptan is one to one; in another it is two to one; and there is always a higher boiling residue which presumably contains products where the ratio of mercaptan to hydrocarbon is greater than two. In order to explain these results the following mechanisms were postulated--I for the additions to styrene, and II for the additions to butadiene.



NOTE: At certain points in this dissertation, indicated by an asterisk, there occur reports of work which was not carried out by the author, but by one or more of the collaborators mentioned on page 1.



The formation of 1-4 addition products with butadiene has been assumed. The structures of these compounds have not been proved. The sulfur compounds used were propyl, lauryl and t-butyl mercaptans, thioglycolic acid and Sharples dodecyl 3B mercaptan (presumably a tertiary triisobutylene mercaptan with the structure:



Preparation of Addition Compounds

The additions of mercaptans to styrene and butadiene are of commercial interest because small amounts of mercaptans are used to promote the copolymerization of these hydrocarbons in the preparation of synthetic rubber. Industrially, this copolymerization is carried out in a soap emulsion. Hence the work here described includes addition reactions carried out in emulsions as well as in homogeneous solutions. The oxidants used were ascaridol for the homogeneous reactions, and potassium persulfate for the reactions in emulsion. Soap was used as the emulsifying agent, and the acid generated by the decomposition of the persulfate was neutralized by a buffer. Table 3 is a list of the sulfides isolated.

A disulfide was isolated only in one instance. Small quantities of dipropyldisulfide ($\text{C}_3\text{H}_7\text{SSC}_3\text{H}_7$) were obtained when propyl mercaptan was added to styrene in emulsion. The formation of this disulfide in emulsion is probably accounted for by the fact that propyl mercaptan is quite soluble in water. Hence a

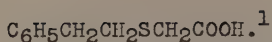
TABLE 3

SULFIDES ISOLATED IN MERCAPTAN ADDITIONS

Mercaptan	Styrene	Butadiene
Propyl	$C_6H_5CH_2CH_2SC_3H_7$ $C_6H_5CHCH_2SC_3H_7$ $CH_2CH_2C_6H_5$	$CH_3CH=CHCH_2SC_3H_7$ $CH_3CH=CHCH_2CH_2CH=CHCH_2SC_3H_7$
Lauryl	$C_6H_5CH_2CH_2SC_{12}H_{25}$ $C_6H_5CHCH_2SC_{12}H_{25}$ $CH_2CH_2C_6H_5$	$CH_3CH=CHCH_2SC_{12}H_{25}$ $CH_3CH=CHCH_2CH_2CH=CHCH_2SC_{12}H_{25}$
Thioglycolic acid	$C_6H_5CH_2CH_2SCH_2C \begin{smallmatrix} O \\ OH \end{smallmatrix}$	$CH_3CH=CHCH_2SCH_2C \begin{smallmatrix} O \\ OH \end{smallmatrix}$
t-Butyl	$C_6H_5CH_2CH_2SC(CH_3)_3$ $C_6H_5CHCH_2SC(CH_3)_3$ $CH_2CH_2C_6H_5$	$CH_3CH=CHCH_2SC(CH_3)_3$ $CH_3CH=CHCH_2CH_2CH=CHCH_2SC(CH_3)_3$
t-Trisobutylene	$C_6H_5CH_2CH_2R$	

fairly high concentration of $C_3H_7S\cdot$ radicals is produced in the aqueous phase of the emulsion by the action of the persulfate on the mercaptan. Under these circumstances there is a much greater probability that these radicals will dimerize to form a disulfide instead of adding as usual to an unsaturated hydrocarbon. Ascaridol in homogeneous solution probably reacts quite slowly with mercaptans to form free radicals. Under these conditions, there is never a high concentration of such radicals, and so the probability of collision with a hydrocarbon molecule is relatively increased.

The one-to-one addition compound of thioglycolic acid and styrene was found to be identical with the compound reported by Holmberg and shown by him to be the abnormal adduct,



Analysis has shown that the compounds isolated in the various reactions mentioned are in fact adducts of mercaptans and olefins as assumed in Table 3 and accounted for by the proposed reaction schemes, I and II, pages 17-18. The analytical data also indicate that the mercaptan to hydrocarbon ratios shown for the various compounds in Table 3 are correct. The styrene derivatives were further characterized by converting them to the corresponding sulfones.

Relative Rates of Oxidations and Additions of Mercaptans

According to the mechanisms postulated (cf. I and II, pp. 17-18) a free mercaptyl radical (RS·) initiates the addition of mercaptans to butadiene or styrene. If this assumption is correct, then the rate of oxidation of any particular mercaptan should be roughly proportional to its rate of addition to the olefins in question. To test this conclusion, the oxidation rates of various mercaptans and their rates of addition were investigated. The expected approximate proportionality was easily demonstrated.

In the first series of oxidation studies, soap emulsions were used. The oxidant was potassium persulfate. The amount of mercaptan oxidized within a given time was measured by titration with silver nitrate. The endpoint was determined amperometrically by Kolthoff's method.² Table 4 gives the results obtained.

The oxidations listed were carried out in a two-phase system, but the oxidant (potassium persulfate) is soluble only in the aqueous phase of that system. Hence the observed oxidation rates can be directly compared only if the solubilities of the

¹Holmberg, op. cit.

²Kolthoff and Harris, Ind. Eng. Chem., Anal. Ed. 18, 161 (1946).

TABLE 4

RATES OF OXIDATION OF MERCAPTANS IN EMULSION

Mercaptan	Time (hrs.)	Temp.	% of Mercaptan Oxidized
Thioglycolic acid	1/60	25°	17
n-Propyl mercaptan	1/2	50°	22
t-Butyl mercaptan	16	50°	35
Lauryl mercaptan	20	50°	10
t-Triisobutylene mercaptan	20	50°	4

various mercaptans in the aqueous phase are approximately equal. The mercaptans actually used are far from meeting this condition. However, the data given do indicate that, for mercaptans of approximately the same solubility (propyl and t-butyl mercaptans or lauryl and t-triisobutylene mercaptans), the primary mercaptan is (in both instances) more easily oxidized than the tertiary one.

To obtain a better comparison of the relative rates of oxidation of these mercaptans, investigations were carried out with single phase systems. An alcoholic solution of mercaptan (1 millimole) and o-phenanthroline (5 millimoles) was added to a glacial acetic acid solution of ferric chloride (3 millimoles).^{*} The mixture was kept at 0°. The colorless ferric ion o-phenanthroline complex forms immediately, but as the ferric ion is reduced by the mercaptan, the solution turns pink due to the formation of the ferrous-o-phenanthroline complex. The intensity of the pink color increases as the reaction proceeds. The elapsed time necessary for the color to reach that of a standard corresponding to 90 per cent reduction of the ferric ion was taken as an indication of the ease of oxidation of the mercaptan. These experiments show that the mercaptans, arranged according to their

relative ease of oxidation, fall in the following order:

Thioglycolic acid » lauryl or propyl mercaptans » t-butyl
or t-triisobutylene mercaptans.

Hence the primary mercaptans are again more easily oxidized than the tertiary mercaptans.

In the first series of addition reactions, styrene was added to propyl and lauryl mercaptans in a soap emulsion. Potassium persulfate was the oxidant. Lauryl mercaptan gave 14 per cent of addition in one hour at 25°, whereas propyl mercaptan gave 52 per cent of addition in one-half hour at the same temperature. Thus the rates of addition of these two mercaptans in emulsion runs parallel to their rates of oxidation under the same conditions.

In the second series of addition reactions, mercaptans were added to butadiene and styrene in homogeneous solution. Ascaridol was the oxidant. Table 5 gives the results of these additions.

TABLE 5
RATES OF ADDITION OF MERCAPTANS IN HOMOGENEOUS SOLUTION

Mercaptan	Hydrocarbon	Ascaridol parts/1000	Time (hrs)	Temp.	Yield %
Thioglycolic acid	Styrene	6	1/6	30°	75
	Butadiene	6	1/6	30°	30
Propyl	Styrene	10	8	50°	21
	Butadiene	10	8	50°	7
Lauryl	Styrene	10	37	50°	53
	Butadiene	10	19	100°	65
t-Butyl	Styrene	10	28	50°	30
t-Triisobutylene	Styrene	10	26	50°	5

For the mercaptans listed, the rates of addition to the hydrocarbon follow the same order as the rates of oxidation in solution.⁹ In all instances, the addition to butadiene is slower than the addition to styrene.

The observed parallelism between the rates of addition and the rates of oxidation indicates that the rate determining step for the addition of a mercaptan to an olefin is very probably the oxidation of the mercaptan to the RS• free radical. (Cf. I and II, pp. 17-18.)

Air and Persulfate as Chain Breakers

Air and persulfate, which in small quantities promote additions to olefins, inhibit the reaction when used in larger quantities.

In order further to elucidate this effect the following experiments were carried out. A sample of soap was prepared from stearic acid which had been carefully freed from peroxides. A sample of peroxide-free styrene was also prepared. Then, in the absence of persulfate, attempts were made to add lauryl mercaptan to both ordinary and peroxide-free styrene in emulsions formed by the purified and unpurified soaps. Parallel experiments (3 hrs. at 30°) were carried out in vacuo¹ and in air. The results are given in Table 6.

These data show that the peroxides in the unpurified reagents catalyze the addition, and that air inhibits the reaction when it is catalyzed only by the organic peroxides present in unpurified soap and styrene.

When persulfate is the only oxidant present in the reaction mixture, the addition is still inhibited by air. The results

¹Experiments carried out in vacuo refer to those in which the procedure described on page 29 was used.

TABLE 6

AIR EFFECT IN THE ABSENCE OF PERSULFATE

Soap Used	Styrene Used	% Addition	
		In vacuo	In air
Unpurified	Purified	15	3.
Unpurified	Unpurified	45	-
Purified	Purified	0	4

in Table 7 were obtained by adding lauryl mercaptan to purified styrene in a peroxide-free soap emulsion. Parallel experiments (3 hrs. at 30°) were carried out in vacuo and in air.

TABLE 7

AIR EFFECT IN THE PRESENCE OF PERSULFATE

Amount K ₂ S ₂ O ₈	% Addition	
	In vacuo	In air
.2 equivalent %	51	13
2 equivalent %	43	11
50 equivalent %	28	16

These figures show that the addition goes faster with .2 equivalent per cent of persulfate (based on the mercaptan used) than it does with a larger quantity of that oxidizing agent. Evidently the persulfate functions not only as a chain initiator but also as a chain breaker. The latter effect may be due to a reaction between the persulfate and either the free radical $C_{12}H_{25}S\cdot$ or the free radical $C_6H_5\dot{C}HCH_2SC_{12}H_{25}$.

The role of the oxygen as a chain breaker for the above additions may be similarly explained. This substance is known to combine rapidly with free radicals. Gomberg remarked on the affinity of oxygen for the free triphenylmethyl radical as early as 1900.¹ Molecular oxygen itself is a di-radical--that is, there are two unshared electrons--one on each atom of the molecule :O:O:. Oxygen in low concentrations, therefore, initiates free radical reactions, whereas, in larger concentrations, it inhibits them by combining with other free radicals and thus breaking the chain.

Catalytic Effect of Disulfides on Mercaptan Additions

The dissociation of disulfides into free radicals was first investigated by Schönberg and his co-workers,² who examined the absorption spectra of these substances. They showed by deviations from Beer's Law that some of these materials (e.g., diphenyldisulfide) were dissociated. Chemical evidence was also found to support this conclusion. At low temperatures α, α' -dithionaphthyldisulfide reacts with silver.



In 1924, G. N. Lewis³ deduced that all molecules which have one or more unshared electrons should be paramagnetic. Any free radical necessarily falls in this class. Hence it is possible to demonstrate the dissociation of a substance into free radicals by determining the magnetic susceptibility and comparing the experimental result with the figure calculated on the basis

¹Gomberg, J. A. C. S. 22, 757 (1900).

²Schönberg, Ber. 66, 1932 (1933).

³Lewis, Valence and Structure of Atoms and Molecules, p. 148, Chem. Cat. Co., New York (1924).

of complete association. In this laboratory, experiments of the type described were carried out with solutions of p-dianisyl disulfide ($p\text{-CH}_3\text{OC}_6\text{H}_4\text{S}$)₂ in toluene.¹ In the dark these solutions showed no evidence of dissociation, but when illuminated, they were definitely dissociated to some extent.

The free radicals formed by the dissociation of a disulfide (RSSR) are free mercaptyl radicals (RS•) of the type which has been assumed to initiate the addition of mercaptans to styrene. Hence if a disulfide which dissociates only when illuminated were added to a mixture of pure (peroxide-free) mercaptan and styrene, no reaction should occur in the dark, but the reaction should proceed under illumination. The experiment was tried with three different disulfides and the expected results were obtained. One mol per cent of disulfide was added to a tube containing an equimolar mixture of pure lauryl mercaptan and styrene.* The tube was then sealed in high vacuum, and allowed to stand at 30°. Under these conditions the addition in the dark usually goes to the extent of 10 to 18 per cent in 2 hours without any catalyst added. This minimal reaction is probably due to small traces of air or peroxide which are extremely difficult to remove from the reaction mixture. Similarly, additions carried out with the indicated quantity of added disulfide also went to that extent. When the reaction tubes were illuminated with a mazda lamp, however, the results given in Table 8 were obtained after 12 hours of reaction at 30°.

The catalytic effect of the disulfide is obvious; dianisyl disulfide is the most effective of those used.

Disulfides were also used to promote the addition of propyl mercaptan to styrene. Here the addition compounds were

¹Mr. John Farr helped with these measurements.

TABLE 8

ADDITION OF LAURYL MERCAPTAN TO STYRENE
PROMOTED BY A DISULFIDE

Disulfide present (1 mol %)	% reaction
None (control)	23
Dianisyl	86
Diphenyl	73
Dithionaphthoyl	42

isolated, and identified (by their boiling points) as the same adducts obtained when ascaridol or persulfate were the oxidants. Table 9 shows the amounts of addition products isolated when 7.6 g. of propyl mercaptan (.1 mol), 10.4 g. styrene (.1 mol), and .001 mol of the disulfide were allowed to react at 50° for 44 hours while illuminated. The large yield of addition product found in the presence of diphenyl and dianisyl disulfides indicates that these compounds are effective promoters for the addition reaction in question.

TABLE 9

DISULFIDE PROMOTED ADDITION OF PROPYL MERCAPTAN TO STYRENE

Materials isolated from reaction mixture	Disulfide			
	None	α, α' -Dithionaphthoyl	Diphenyl	Dianisyl
Propyl mercaptan	5.3 g.	5.0 g.	.6 g.	.3 g.
Styrene	8.1	7.8	.4	.6
1:1 adduct	2.9	3.3	13.5	15.2
Residue (2:1 adduct, etc.)	1.9	1.8	3.1	1.3

EXPERIMENTAL PART

Reagents

Butadiene: The butadiene used was obtained from the Carbide and Carbon Corporation. It was distilled (b.p. -4°) to free it from the antioxidant with which it had been stabilized.

Styrene: The styrene used was obtained from the Dow Chemical Company. It was distilled away from the antioxidant under reduced pressure (b.p. $48^{\circ}/^{12}$ mm.). In certain instances it was poured directly into the reaction vessels; in others it was distilled into these vessels on the vacuum line.

Mercaptans: Lauryl and propyl mercaptans were made from the corresponding bromides by treatment with thiourea.¹ The intermediate isothiuronium salts were purified by recrystallization from benzene. The p-anisyl mercaptan was prepared from p-anisidine by way of the corresponding diazonium salt.² Thioglycolic acid (Eastman Kodak Company) and triisobutylene mercaptan (Sharples Corporation) were purified by distillation under reduced pressure. t-Butyl mercaptan was obtained from the Rubber Reserve Board and purified by distillation.

<u>Mercaptan</u>	<u>Boiling Point</u>
Lauryl	$84-85^{\circ}/^1$ mm.
Propyl	$67-68^{\circ}$
t-Butyl	$64-64.5^{\circ}$
t-Triisobutylene	$69-70^{\circ}/^1$ mm.

¹Organic Synthesis, 21, 56.

²Suter and Hansen, J. A. C. S., 54, 4100 (1932).

<u>Mercaptan</u>	<u>Boiling Point</u>
Thioglycolic acid	123°/ ²⁹ mm.
p-Anisyl	88-90°/ ⁵ mm.

Disulfides: Dianisyl and diphenyl disulfides were prepared by oxidizing the corresponding mercaptans with iodine.¹ Dithionaphthoyl disulfide was prepared from α -naphthyl magnesium bromide and carbon disulfide.²

<u>Disulfide</u>	<u>Melting Point</u>
Diphenyl	61°
α, α' -Dithionaphthoyl	169°
Dianisyl	42.5-43.5°

Determination of Mercaptan

The amount of mercaptan utilized in any experiment was determined by titrating the reaction mixture (or an aliquot thereof) against standard silver nitrate solution. The end point was determined amperometrically.³

Evacuation and Degassing Process

For those reactions designated as having been carried out in vacuo, the following procedure was used: The reaction mixture, before the hydrocarbons were added, was frozen to -80° on the vacuum line and evacuated to 10^{-5} mm. The vessel was then shut off from the pumping system and allowed to warm up to room temperature. This process was repeated at least three times. Styrene (except when unpurified materials are specified) was similarly treated and then distilled on the vacuum line into the reaction mixture.

¹Hübner and Alsberg, Ann. 156, 330 (1870).

²Houben, Ber. 39, 3229 (1906).

³Kolthoff and Harris, op. cit.

Addition of Mercaptans to Styrene and Butadiene

1. In Emulsion

Potassium persulfate (.03 moles) was dissolved in 300 cc of an aqueous buffer solution containing sodium carbonate (13 g.) and sodium bicarbonate (1 g.). Ivory soap flakes (4 g.) and .12 moles each of the mercaptan and hydrocarbon were then added to the persulfate solution contained in a citrate (pressure) bottle. The bottle was equipped with a wire clamp to hold the rubber stopper securely in place. When butadiene was used, the bottles were cooled in an ice-salt bath before the hydrocarbon was added. The reaction mixtures were shaken in a thermostat at 50°. To determine the time required for complete utilization of the mercaptan, several small scale experiments with the same reaction mixture were carried out simultaneously. These were stopped at intervals and the unreacted mercaptan was determined by titration. When the reaction was almost complete, the large vessels were cooled and opened. Dilute hydrochloric acid was added to break the emulsion. The addition products and the stearic acid (formed by acidification of the soap) were extracted with benzene. A trace of hydroquinone was added to the benzene solution. The various components of this extract were then separated by fractional distillation in vacuo. Some difficulty was experienced whenever one of the addition products boiled at approximately the same point as stearic acid. In these instances, the stearic acid fraction was dissolved in alcohol and made alkaline with sodium hydroxide; calcium stearate was then precipitated by the addition of calcium chloride. The calcium soap was removed by centrifuging the mixture and the addition compound was isolated from the alcohol solution by distillation.

Sulfones were obtained by oxidizing 1 g. of the corresponding sulfide in glacial acetic acid (1 cc.) with 30 per cent hydrogen peroxide (2 g.). The mixture was heated on the steam bath for one-half hour. The solid sulfone which separated when the mixture was cooled, was collected on a filter. It was dried in air and recrystallized from ethyl alcohol.

2. In Homogeneous Solution

Ascaridol (1 mol per cent) was added to equimolar quantities of mercaptan and hydrocarbon. The reaction vessels were cooled and sealed and then kept at 50° for several days. When the tubes were opened, a trace of hydroquinone was added to the reaction product, and the mixture fractionally distilled in vacuo.

Table 10 gives the properties of the new addition compounds prepared.

The only adduct isolated from thioglycolic acid and styrene had practically the same melting point (55-56°) as that prepared by Holmberg (57°) and shown by him to be the abnormal addition product.¹ The corresponding sulfone melted at 75-76° in agreement with the value given by Holmberg (77°).

Rates of Oxidation in Emulsion

A solution containing potassium persulfate (.15 g.) and sodium hydroxide (.11 g.) in 40 cc. of a borate-carbonate buffer (pH = 10)² was added to a solution of stearic acid (.3 g.) and mercaptan (1.25 millimoles) in 10 cc. of benzene. The mixture was shaken in a glass-stoppered flask held at the required temperature in a thermostat. The unreacted mercaptan was determined by titration in the manner already described.

¹Holmberg, op. cit.

²Clark, Determination of Hydrogen Ions, p. 215. Willison and Wilkins, Baltimore (1922).

TABLE 10

PROPERTIES OF NEW ADDITION COMPOUNDS¹

Compound	Boiling point	Melting point
$C_6H_5CH_2CH_2SC_3H_7$	128-129°/10 mm	50-51°
$C_6H_5CH_2CH_2SO_2C_3H_7^*$		
$C_6H_5CHCH_2SC_3H_7$ $CH_2CH_2C_6H_5$	173-176°/1 mm	57-58°
$C_6H_5CHCH_2SO_2C_3H_7^*$ $CH_2CH_2C_6H_5$		
$CH_3CH=CHCH_2SC_3H_7$	52-53°/10 mm	75-76°
$CH_3CH=CHCH_2CH_2CH=CHCH_2S-C_3H_7^*$	114-117°/10 mm	
$C_6H_5CH_2CH_2SC_{12}H_{25}$	184-187°/10 mm	
$C_6H_5CH_2CH_2SO_2C_{12}H_{25}^*$		
$C_6H_5CHCH_2SC_{12}H_{25}$ $CH_2CH_2C_6H_5$	not distilled	61-63°
$C_6H_5CHCH_2SO_2C_{12}H_{25}^*$ $CH_2CH_2C_6H_5$		
$CH_3CH=CHCH_2SC_{12}H_{25}$	146-149°/1 mm	107-108°
$CH_3CH=CHCH_2CH_2CH=CHCH_2SC_{12}H_{25}$	179-185°/1 mm	
$CH_3CH=CH-CH_2SCl_2COOH$	110-114°/4 mm	
$C_6H_5CH_2CH_2SC(CH_3)_3$	138-140°/17 mm	
$C_6H_5CH_2CH_2SO_2C(CH_3)_3^*$		
$C_6H_5CH_2CH_2SC(CH_3)_3$ $CH_2CH_2C_6H_5$	166-169°/1 mm	
$CH_3CH=CHCH_2SC(CH_3)_3$		
$CH_3CH=CHCH_2CH_2CH=CHCH_2SC(CH_3)_3$		
$C_6H_5CH_2CH_2SR^2$	134-138°/1 mm	

¹C and H analyses by Dr. T. S. Ma.²R = t-triisobutylene group.

TABLE 10--Continued

% C		% H		% S	
Calc'd	Found	Calc'd	Found	Calc'd	Found
73.26	72.85	8.95	8.90	17.78	18.46
				15.07	14.75
80.24	79.19	8.51	8.13	11.27	11.43
				10.13	10.23
64.57	64.38	10.94	10.48	24.62	24.49
71.68	71.56	10.94	10.67	17.10	17.97
78.37	79.62	11.18	11.03	10.46	10.98
70.46	70.47	10.13	9.66	9.47	9.16
				7.42	7.82
74.91	75.94	12.58	12.46		
77.33	77.77	12.33	12.01		
49.30	48.92	6.91	6.92	21.94	22.20
63.68	63.36	8.02	7.93		
78.37	78.03	11.18	11.91	10.42	10.37

Rates of Addition in Emulsion

The procedure was the same as that used in determining the rates of oxidation (described above), except that styrene (1.25 millimoles) was also added to the benzene solution of the mercaptan.

Rates of Addition in Solution

Equimolar quantities of hydrocarbon and mercaptan were allowed to react in sealed tubes in the presence of ascaridol (one mol per cent). The unused mercaptan was determined by titration.

Determination of Air Effect

The additions in vacuo and in the presence of air were carried out with the same quantities of materials described above for the experiments on the rates of addition in emulsion. Redistilled water was used in the buffer. Unpurified stearic acid refers to the U. S. P. grade and unpurified styrene refers to material which had been distilled once at reduced pressure and then introduced into the reaction mixture without further precautions.

Purified stearic acid refers to material which had been treated as follows: Stearic acid (U. S. P.) dissolved in benzene was shaken with three portions of an aqueous acid solution of ferrous sulfate (to remove peroxide). The benzene was distilled off and the stearic acid distilled at reduced pressure. The solid material was kept in a dry box under nitrogen. Here it was powdered, weighed, and added to the reaction vessels as required. Purified styrene refers to material which had been freed of peroxides by shaking it with ferrous sulfate. It was distilled at reduced pressure and re-distilled on the vacuum line directly into the reaction vessel.

The mercaptan was placed in a small cup sealed into the reaction flask. Thus it was not in contact with the reaction mixture during the evacuation and degassing process.

For the experiments run in the presence of air the reaction mixtures were also carried through the evacuation and degassing process. Before the tubes were sealed off, however, air was admitted into them.

The Effect of Disulfides

1. Lauryl mercaptan addition. One mol per cent of the disulfide was added to an equimolar mixture of styrene and lauryl mercaptan in a reaction tube. The solution was frozen to -80° and then evacuated and degassed. The tubes were sealed off and allowed to react at 30° for 12 hours. The unused mercaptan was determined by titrating the mixture.

2. Propyl mercaptan addition. The procedure used was the same as that described for lauryl mercaptan. The reaction products were isolated by distilling the reaction mixture.

SUMMARY

1. The literature concerning free radical chain reactions in solution has been reviewed.

2. A free radical chain mechanism has been proposed for the addition of mercaptans to styrene and butadiene.

3. Lauryl, propyl, t-butyl, t-triisobutylene mercaptans and thioglycolic acid have been added to butadiene and styrene. The products obtained are in conformity with the proposed mechanism.

4. The rates of oxidation of the mercaptans are parallel to their rates of addition to the hydrocarbons in question.

5. Oxygen and persulfate, when present in large quantities, act as chain breakers for the addition reaction.

6. Those disulfides, which, when illuminated, dissociate into free mercaptyl radicals, promote the addition of mercaptans to olefins.

PART II

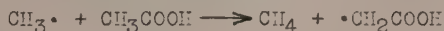
DECOMPOSITION OF ACETYL PEROXIDE IN ALDEHYDES

INTRODUCTION

The present work deals with the reactions which occur when diacetyl peroxide dissolved in n-butyraldehyde is decomposed by heat. Previous experience with other solvents has shown, that under these conditions, free methyl and free acetoxyl radicals are formed. The products isolated can be accounted for by assuming that these free radicals react with the molecules of the solvents, hence it is advantageous to outline earlier work in this field before considering the experimental results here obtained.

It has been demonstrated that when free radicals are generated in solution, they react in various different ways:

1. Reaction with the solvent to form a new radical



2. Re-arrangement or decomposition to form a new radical



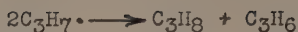
3. Dimerization



4. Disproportionation²

¹Kharasch and Gladstone, J. A. C. S. 65, 15 (1943).

²McDay, Doctor's Thesis, University of Chicago (1945).



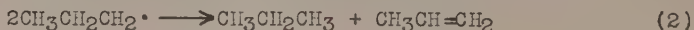
In reactions (1) and (2) new free radicals are formed; in reactions (3) and (4) no such new radicals are obtained.

On the basis of the work already carried out, it is possible to make certain generalizations which help to predict the behavior of a given free radical under specified conditions. Radicals with a high energy content easily extract a univalent atom from a molecule of the solvent. The half life of these radicals is therefore short, and they seldom exist in concentrations large enough to permit dimerization. For example, methyl radicals in solution usually extract an atom of hydrogen from the solvent molecule, or if that is not available, an atom of chlorine. Thus, they form new radicals.



In solution free methyl radicals have never been observed to decompose or give disproportionation products such as ethylene.

Free propyl radicals either disproportionate or combine with a hydrogen atom from a neighboring molecule.



Where pure ether is the solvent only the second of these reactions occurs. When a molecule of the solvent contains a hydrogen atom which is easily removed only the first reaction occurs--as will be shown later. With other solvents such as isopropylbenzene, both reactions occur.

Free radicals stabilized by resonance exist long enough to dimerize. Thus, when methyl radicals are generated in acids,¹

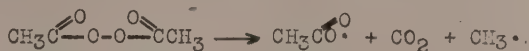
¹Kharasch and Gladstone, op. cit.

esters,^{1,2} nitriles,³ etc., the new free radicals formed from the solvent (equation 1) usually dimerizes (equation 3).

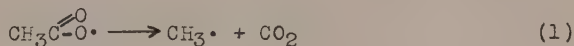
Free radicals such as butyryl, $C_3H_7C(=O)\cdot$ will be shown to decompose as indicated in equation 2, page 38.

The decomposition of various organic peroxides has been frequently used as a source of free radicals. Benzoyl,¹ and lauryl¹ peroxides have been so decomposed, but most of the work of this nature has been carried out with acetyl peroxide.^{1,2,3,4} The further discussion in this paper will be confined to that substance.

It has been postulated that the initial step in the decomposition of acetyl peroxide is:⁵



Usually, when the molecule of solvent contains an atom of hydrogen, methane is formed (see equation 1, page 38). In most instances, however, carbon dioxide and methane are produced in larger quantities than is indicated by the above equation--that is, among the reaction products, there is more than one mol of each of these substances for each mol of peroxide decomposed. This fact indicates that the free acetoxyl radical further decomposes to give additional molecules of carbon dioxide and more free methyl radicals.



¹McBay, op. cit.

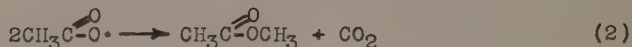
²Jensen, Doctor's Thesis, University of Chicago (1944).

³Smith, Master's Thesis, University of Chicago (1945).

⁴Kharasch and Gladstone, op. cit.

⁵Hey and Waters, Chem. Reviews 21, 189 (1937).

Since methyl acetate usually occurs among the reaction products, it has been postulated¹ that the acetoxy free radical also reacts as follows:



Methyl acetate may also be formed by the reaction of the acetoxy free radical with a molecule of the peroxide.



These hypotheses are strengthened by the facts that, in the decompositions in question, there is usually more carbon dioxide formed than methane, and that the amount of methyl acetate isolated is approximately equivalent to the excess of carbon dioxide.

The direct combination of free methyl and acetoxy radicals to form methyl acetate ($\text{CH}_3\cdot + \text{CH}_3\text{C}(=\text{O})\text{O}\cdot \longrightarrow \text{CH}_3\text{C}(=\text{O})\text{OCH}_3$) is improbable, since the concentration of the free acetoxy radical is low compared to that of the solvent. The concentration of free methyl radicals is also low because of the great activity of these radicals.

The free methyl radical always extracts an atom from a molecule of the solvent to give a new free radical. Where a hydrogen atom is not available (trichloroacetyl chloride),² then an atom of chlorine is



Even here, however, some methane is produced by the removal of hydrogen atoms from molecules of undecomposed peroxide.

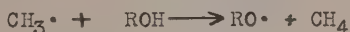
¹Jensen, op. cit.

²McKay, op. cit.

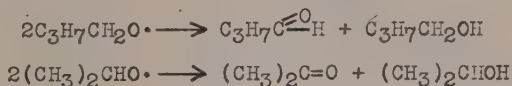
All the free radicals derived from the solvents which were investigated prior to the work here reported, either dimerized or combined with other free radicals derived from the solvent. Table 1 lists the reaction products formed in some of these instances. Examination of this table shows that the free methyl radical exhibits a high degree of selectivity in the extraction of a univalent atom from a molecule of the solvent. Only one particular univalent atom is extracted from a molecule of each solvent listed. These atoms arranged in order of their ease of removal by the free methyl radical are as given in Table 1.

In some instances,¹ molecules of the products formed by dimerization have an atom more easily removable than any atom in the solvent molecule. In such instances, the dimeric product, even though its concentration is much lower than that of the original solvent, is preferentially attacked; thus, trimeric or tetrameric products of the solvent are formed.

The recent work of Rowe² gives examples of other ways (besides dimerization) in which a free radical formed from the solvent may react. Rowe decomposed acetyl peroxide in a series of alcohols. He has suggested that free methyl radicals attack such solvents as follows:



When the alcohol is primary or secondary, the $\text{RO}\cdot$ radical disproportionates:



¹Kharasch and Gladstone, op. cit.

²Rowe, Doctor's Thesis, University of Chicago (1946).

TABLE 1

DIMERIZATION OF SOLVENT FREE RADICALS

Solvent	Product	Reference
CH_3COOH	$\begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{CH}_2\text{COOH} \end{array}$	1
CH_2ClCOOH	$\begin{array}{c} \text{CHClCOOH} \\ \\ \text{CHClCOOH} \end{array}$	1
$(\text{CH}_3)_2\text{CHCOOH}$	$\begin{array}{c} (\text{CH}_3)_2\text{C}-\text{COOH} \\ \\ (\text{CH}_3)_2\text{C}-\text{COOH} \end{array}$	1
$\text{ClCH}_2\text{COOCH}_3$	$\begin{array}{c} \text{CHClCOOCH}_3 \\ \\ \text{CHClCOOCH}_3 \end{array}$	3
$\text{FCH}_2\text{COOCH}_3$	$\begin{array}{c} \text{CHF}\text{COOCH}_3 \\ \\ \text{CHF}\text{COOCH}_3 \end{array}$	3
$(\text{CH}_3)_2\text{CHCOCl}$	$\begin{array}{c} (\text{CH}_3)_2\text{CCOCl} \\ \\ (\text{CH}_3)_2\text{CCOCl} \end{array}$	3
$\text{C}_2\text{H}_5\text{CN}$	$\begin{array}{c} \text{CH}_3\text{CHCN} \\ \\ \text{CH}_3\text{CHCN} \end{array}$	4
CH_3CN	$\begin{array}{c} \text{CH}_2\text{CN} \\ \\ \text{CH}_2\text{CN} \end{array}$	4
$\text{C}_6\text{H}_5\text{CH}_2\text{CN}$	$\begin{array}{c} \text{C}_6\text{H}_5\text{CHCN} \\ \\ \text{C}_6\text{H}_5\text{CHCN} \end{array}$	4
CCl_3COCl	$\begin{array}{c} \text{Cl}_2\text{CCOCl} \\ \\ \text{Cl}_2\text{CCOCl} \end{array}$	2
$\text{CHCl}_2\text{COOCH}_3$	$\begin{array}{c} \text{Cl}_2\text{CCOOCH}_3 \\ \\ \text{Cl}_2\text{CCOOCH}_3 \end{array}$	2
$\text{CH}_3\text{COOCH}_3$	$\begin{array}{ccc} \text{CH}_2\text{COOCH}_3 & & \text{CH}_2\text{COOCH}_3 \\ & & \\ \text{CH}_2\text{COOCH}_3 & & \text{CH}-\text{COOCH}_3 \\ & & \\ & & \text{CH}_2\text{COOCH}_3 \end{array}$	2
$\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$	$\begin{array}{c} \text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \\ \\ \text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \end{array}$	2

TABLE 1--Continued

Solvent	Product	Reference
$C_6H_5CH_2CH_3$	$C_6H_5CHCH_3$ $C_6H_5CHCH_3$	2
$C_6H_5CH(CH_3)_2$	$C_6H_5C(CH_3)_2$ $C_6H_5C(CH_3)_2$	2
$p-OCH_3C_6H_4CH_2CH_2CH_3$	$p-OCH_3C_6H_4CHCH_2CH_3$ $p-OCH_3C_6H_4CHCH_2CH_3$	2
$(CH_3)_3CCOOH$	$CH_2C(CH_3)_2COOH$ $CH_2C(CH_3)_2COOH$	2

¹Kharasch and Gladstone, op. cit.²McBay, op. cit.³Jensen, op. cit.⁴Smith, op. cit.

DISCUSSION OF RESULTS

Preliminary work on the decomposition of acetyl peroxide dissolved in isobutyraldehyde¹ showed that carbon monoxide and propane are among the reaction products formed. In order to further investigate the decomposition of peroxides in aldehydes, acetyl peroxide was decomposed in n-butyraldehyde at the boiling point of the aldehyde (75°). The reaction took place over a period of twelve hours. Table 2 shows the products obtained.

TABLE 2
DECOMPOSITION OF ACETYL PEROXIDE IN n-BUTYRALDEHYDE

Reagents	No. of Moles	No. of Moles per Mole of Peroxide
n-Butyraldehyde used	2.750	7.971
Acetyl peroxide used	.345	1.000
n-Butyraldehyde recovered	1.260	3.652
n-Butylaldehyde decomposed	1.490	4.319
Products		
Carbon dioxide	.543	1.574
Methane	.528	1.530
Carbon monoxide	.770	2.232
Propane	.779	2.258
Acetic acid	.116	.336
Acetic ester	.03 (app.)	.09 (app.)
Butyric acid	.115	.333
Ester	.03 (app.)	.09 (app.)
Dibutryl	.018	.052
High boiling residue	25.26 grams	

It is of interest to note, first, that no methyl acetate was formed, but that a considerable quantity of acetic acid was

¹McBay, op. cit.

isolated. This fact suggests that the acetoxyl free radical extracts a hydrogen atom from a molecule of the solvent. Most of the solvents previously used, contained no hydrogen atoms sufficiently labile to be removed by the acetoxyl free radical, which has relatively little energy. Reactions (1), (2), and (3) on pages 39 and 40, have hitherto accounted for most of this radical. The aldehydic hydrogen, however, is extremely active, and is therefore readily removed by the acetoxyl free radical. The acetic acid thus formed, together with the acetic ester and the gaseous carbon dioxide evolved account completely for the $\text{C}-\overset{\text{O}}{\text{O}}-\overset{\text{O}}{\text{C}}$ portion of the acetyl peroxide.

Removal of the aldehydic hydrogen from molecules of the solvent (by either the free acetoxyl or free methyl radicals) should result in the formation of the free butyryl radical:



This free butyryl radical may then undergo a number of different reactions.

1. Some of it may dimerize to give 4-5-diketoöctane.

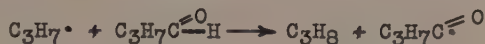


2. Some of it may lose carbon monoxide to give the free propyl radical.



As a matter of fact 4,5-diketoöctane was identified among the reaction products. A larger amount of the free butyryl radical reacted according to equation (2). Carbon monoxide and propane were found among the reaction products in equimolar quantities. No propene was present. Hence the propane cannot have been

formed by the disproportionation of the free propyl radical. It was probably formed by the attack of the free propyl radical on the exceedingly reactive aldehydic hydrogen atoms.



An acetic ester and a higher boiling ester with a saponification equivalent of 147 were also isolated. Neither of these has as yet been further identified. Their boiling points and indices of refraction suggest that they may be butyl acetate and butyl butyrate, respectively. No explanation is here offered to account for the formation of these esters, or of the butyric acid also isolated.

The high boiling residue contained fractions with a molecular weight (227) close to that of a trimer of butyraldehyde (216). Higher fractions (molecular weight 353) may contain some form of aldehyde pentamer (molecular weight 360). These materials contained some ester groups, but no hydroxyl groups. The lower fractions absorbed hydrogen at room temperature (Adam's catalyst). Probably a considerable portion of these high boiling fractions are polymers of butyraldehyde formed when this substance is heated in the presence of acetic acid. Some of the high boiling material, however, probably results from reactions of the free butyryl radical which are as yet unknown.

EXPERIMENTAL PART

Decomposition of the Peroxide

Reagent grade n-butyraldehyde (Eastman) was distilled through an efficient fractionating column (b.p. 74-75°). Dry acetyl peroxide (39.5 g., .345 moles) was prepared, and 51.7 g. of the aldehyde added to it. This solution was added over a period of three hours to 146.3 g. of n-butyraldehyde held at boiling temperature in an apparatus which had previously been flushed with nitrogen gas to remove all oxygen. The procedure and apparatus used in this part of the work were those described by McBay.¹ The reaction (as indicated by the evolution of gas) was completed in 12 hours. The gas collected (exclusive of carbon dioxide which was absorbed by soda lime tubes) amounted to 1.64 moles.

Analysis of Gas

The average molecular weight of the gas (Regnault method) was 27.2. A sample of the gas was cooled to -190° (liquid nitrogen) and the constituents volatile at that temperature were pumped off. The solidified material was then allowed to return to the original temperature of the sample. The pressure of the gas so obtained showed that it amounted to 21.3 per cent of the original sample. Its molecular weight (42.8) indicated that it was mostly propane (mol. wt. 44). This gas was passed through concentrated sulfuric acid several times. The fact that none of it was absorbed indicated that it contained no propene. The proportion

¹Op. cit.

of carbon monoxide in the original gas (47.0 per cent) was determined by absorption in an ammoniacal solution of cuprous chloride contained in a Morehead apparatus. The remaining gas (31.7 per cent) was assumed to be methane. The average molecular weight of the original gas calculated from these figures is 27.6, which agrees closely with the experimentally determined value of 27.2.

Identification of Liquid Reaction Products

The cold traps were slowly warmed to 35°. The gas given off during this procedure contained 18.9 grams of propane (molecular weight 44.4). The residual liquid proved to be butyraldehyde (b.p. 74-75°, $n_D^{20} = 1.3819$).

The bright yellow liquid remaining in the reaction flask was fractionated through a small Podbielniak column. Most of the aldehyde was removed at atmospheric pressure. Distillation was then continued at 145 mm. Fractions later shown to contain acetic acid and an acetic ester were so removed. The pressure was then reduced to 25 mm. and the distillation continued. Fractions later shown to contain butyric acid, dibutyl, and an ester were thus obtained.

The acetic and butyric acids were identified as their p-bromophenacyl esters.¹ The acetic ester (m.p. 84-85°) did not depress the melting point (85°) of an authentic sample of p-bromophenacyl acetate. The butyric ester (m.p. 61-62°) did not depress the melting point of an authentic sample of p-bromophenacyl butyrate.

The fractions containing acetic acid were combined, and the acid removed by washing the liquid with sodium bicarbonate solution. The residual liquid was distilled (b.p. 66-70°/150 mm),

¹Shriner and Fuson, Identification of Organic Compounds, pp. 97, 144, John Wiley and Sons, New York (1935).

$n_D^{20} = 1.3989$). The distillate was treated with p-toluidine¹ and acetyl p-toluidide was obtained (m.p. 147°). This material did not depress the melting point (147°) of an authentic sample of acetyl p-toluidide.² This fact indicates that the residual liquid was an acetic ester, probably butyl acetate ($n_D^{20} = 1.3951$).

A portion of the fraction suspected (from its bright yellow color) to contain dibutyril was treated with hydroxylamine hydrochloride.³ A crystalline dioxime (m.p. 177-179°) was thus obtained. This value agrees fairly well with the value (181°) given in the literature. The fractions containing dibutyril also contained butyric acid and an ester. These fractions were combined, and the diketone reduced with hydrogen over platinum (Adam's catalyst). The mixture was freed from acid by washing with sodium carbonate solution. The ester was then distilled (b.p. 72-78/²⁵ mm). The residual liquid was presumed to consist entirely of glycol formed from the diketone; its quantity afforded a measure of the amount of dibutyril produced in the reaction. The saponification equivalent of the distillate was 147. This fact indicates that it may be butyl butyrate (saponification equivalent 144).

High Boiling Residue

The undistilled material from the reaction mixture was fractionated on a molecular still. No residue remained behind. The following fractions were obtained:

¹Koelsch, J. A. C. S. 55, 3049 (1933).

²Shriner and Fuson, op. cit., p. 97.

³Ibid., p. 145.

Fraction	Wt. (grams)	n_D^{20}	Mol. wt.
1	2.20	1.4443	227
2	7.11	1.4495	
3	8.88	1.4569	
4	3.07	1.4685	353

The molecular weights indicate that fractions 1 and 4 are, respectively, trimeric and pentomeric with respect to butyraldehyde. Fraction 1 gave a negative test for hydroxyl groups. When this material was hydrogenated at room temperature (Adam's catalyst) it absorbed .6 molecules of hydrogen per molecule. After hydrogenation .6-.7 OH groups were present per molecule. It had a saponification equivalent of 200, that of fraction 2 was 193.

SUMMARY AND CONCLUSIONS

1. The possible reactions of free radicals in solution are discussed.

2. Acetyl peroxide was decomposed when dissolved in n-butyraldehyde. Carbon dioxide, methane, acetic acid, butyric acid, dibutyl, some unidentified esters, and equimolar quantities of carbon monoxide and propane were obtained. High boiling residues were also formed.

3. About one half of the butyryl free radicals generated in this reaction decompose into carbon monoxide and propyl radicals. A portion of the remainder dimerizes.

4. The exclusive formation of acetic acid and propane by the action of the free acetoxyl and propyl radicals respectively, indicates that the aldehydic hydrogen in n-butyraldehyde is very easily removed by free radicals.

5. High boiling products are formed. These may be in part ordinary polymerization products of the aldehyde; however, some high boiling esters are also present.

